

PATENT SPECIFICATION

784,843



Date of Application and filing Complete Specification: Dec. 21, 1954.
No. 36945/54.

Application made in Germany on Dec. 21, 1953.

Application made in Germany on June 14, 1954.

Complete Specification Published: Oct. 16, 1957.

Index at acceptance:—Class 2(4), D1T.

International Classification:—C09b.

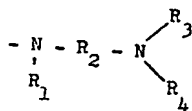
COMPLETE SPECIFICATION

New Basic Phthalocyanine Dyestuffs and a process for their Production

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen - Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new basic phthalocyanine dyestuffs and to a process of making the same.

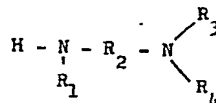
The present invention provides new basic phthalocyanine dyestuffs having from one to four radicals of the general formula



attached to a phthalocyanine radical, wherein R_1 is a hydrogen atom or an alkyl radical, R_2 is an acyclic bivalent radical, and R_3 and R_4 are aliphatic radicals or together with the

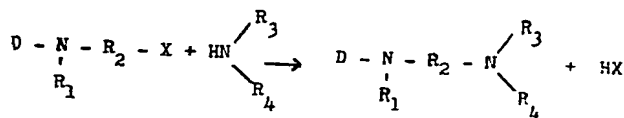
adjacent nitrogen atom form a heterocyclic ring.

The present invention also provides a process for the production of these new basic dyestuffs, which comprises reacting a phthalocyanine dyestuff containing one to four replaceable halogen atoms with a tertiary amine of the general formula



wherein R_1 to R_4 have the aforementioned meanings.

The phthalocyanine dyestuff containing one to four replaceable halogen atoms can alternatively be reacted with an aliphatic primary or secondary amine containing at least one halogen atom, the halogen compound obtained in this reaction being subsequently reacted with a secondary amine. The reaction underlying this process in accordance with the invention can be illustrated by the following equation:



wherein D is a phthalocyanine radical, R_1 is hydrogen or an alkyl radical, R_2 is an acyclic bivalent radical, R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring, and X is a halogen atom. If R_1 is an acyclic bivalent radical carrying a halogen atom, a product is obtained in which there are two acyclic bi-

valent radicals carrying $-\text{N} \begin{array}{c} \text{R}_3 \\ \diagup \\ \text{R}_4 \end{array}$ radicals.

According to the invention, also, in the dyestuff produced R_2 can be an acyclic bivalent radical which contains an $-\text{N} \begin{array}{c} \text{R}_3 \\ \diagup \\ \text{R}_4 \end{array}$ radical.

BEST AVAILABLE COPY

Instead of using phthalocyanine dyestuffs it is possible to use dyestuff intermediates containing a replaceable halogen atom, which upon completion of the above reactions are converted into the final phthalocyanine dyestuff.

Examples of dyestuff derivatives containing replaceable halogen which are suitable as starting materials for the processes of the invention are phthalocyanine dyestuffs containing a carboxylic acid halide, or a sulphonic acid halide group, or a halogenoalkyl group, such as an ω -chloromethyl group.

Examples of suitable aliphatic tertiary amines containing primary or secondary amino groups are 1-amino-2-dimethyl-aminoethane, 1-amino-3-dimethylamino-propane, 1-diethylamino-3-amino-*n*-pentane and the amide of methylaminoacetic acid and 1-diethylamino-4-amino-*n*-pentane.

Examples of suitable aliphatic primary or secondary amines containing halogen atoms are β -chloro-ethylamine, β,γ -dibromopropylamine, 1-amino-4-chlorobutane, and β,β' -dichloro-diethylamine.

Among the secondary amines which can be reacted with the halogen atom to form the tertiary amine grouping are all common secondary amines, as for example dimethylamine, diethylamine, diethanolamine, piperidine, pyrrolidine and pyrroline.

An excess of the organic base employed in the reaction, or an inert organic solvent, such as benzene or acetone, can be used as a reaction medium. It is often of advantage to carry out the reaction in an aqueous suspension.

The hydrogen halide set free in the reaction can be bound by using an excess of the base or by adding another acid binding agent to the reaction mixture, such as an alkali metal carbonate, sodium hydroxide or sodium bicarbonate.

If the reaction is carried out in an aqueous suspension it may be of advantage to add a catalytic amount of pyridine. The reaction then proceeds more quickly.

Temperatures of 0—100°C. have proved to be advantageous for obtaining the best results.

The invention can be carried out by mixing the halogen-containing dyestuff, for example copper phthalocyanine-(3)-di- and tri-sulphochloride, with the amine, as for example 1-amino-2-dimethylaminoethane, while stirring.

Examples of suitable reaction media are water, an inert organic solvent or an excess of the organic base. Preferably the reaction mixture is stirred for some hours at room temperature while the basic phthalocyanine dyestuff formed is precipitating. To complete the reaction the mixture can be heated for a short time to 60—100°C. The basic dyestuff formed can be recovered from the reaction mixture by filtration.

Some of the basic phthalocyanine dyestuffs

obtainable by the process of this invention are soluble in organic solvents, such as ethyl alcohol, benzyl alcohol, esters, aromatic hydrocarbons and dimethyl formamide, and can be used for dyeing plastics and varnishes or in offset printing.

The high affinity of the new basic phthalocyanine dyestuffs to fibres derived from various raw materials makes these dyestuffs, especially in form of their water-soluble salts, extremely suitable for dyeing cotton, wool, cellulose, regenerated cellulose, fibres of polyamides or polyacrylonitrile, paper, or paper raw materials such as paper pulp. The basic phthalocyanine dyestuffs take on these materials very easily from a dilute acid solution and the resulting dyeings show extremely good wet fastness.

It is very surprising that phthalocyanine dyestuffs will become readily soluble in dilute acids such as acetic acid if at least one tertiary amino group is introduced into the molecule.

The following Examples, in which all parts are by weight, further illustrate the invention.

EXAMPLE 1:

To a solution of 10 parts of copper phthalocyanine in 100 parts of chlorosulphonic acid, 21 parts of thionyl chloride are slowly added at a temperature of 60—70°C. The reaction mixture is then heated for 4—5 hours to 112—113°C. until a sample is soluble in a 10% solution of pyridine and is insoluble in aqueous diethylamine. The reaction mixture is cooled and poured on to ice. The precipitated copper phthalocyanine-(3)-di- and tri-sulphochloride is filtered off with suction and washed with ice water until it gives a neutral reaction.

The paste of the sulphochloride thus obtained is added to a solution of 10.72 parts of 1-amino-2-dimethylaminoethane in 38.5 parts of water, stirred for 12 hours at room temperature and then for one hour at 60°C. The basic dyestuff formed is filtered off and washed with hot water. It dissolves in dilute acetic acid to give a clear greenish-blue solution.

By using the nickel phthalocyanine instead of the copper phthalocyanine a dyestuff is formed which is soluble in dilute acetic acid to give a more greenish-blue solution. (To obtain the sulphochloride of the nickel phthalocyanine the reaction mixture has to be heated for 5 hours to 117—118°C.).

Instead of the 1-amino-2-dimethylaminoethane there may be used equimolecular amounts of 1-amino-3-dimethylamino-propane, 1-diethylamino-4-amino-*n*-pentane, or the amide of methylaminoacetic acid and 1-diethylamino-4-amino-*n*-pentane. The basic dyestuffs obtained are soluble in dilute acetic acid to give a clear greenish-blue solution.

EXAMPLE 2:

To a solution of 9.96 parts of the sodium salt of copper phthalocyanine-4,4'-disulphonic acid (obtained by the reaction of two mols of phthalic acid anhydride and two mols

of the sodium salt of 4-sulphophthalic acid in a urea melt) in 100 parts of chlorosulphonic acid, 6.2 parts of thionyl chloride are added drop by drop at a temperature of 60—70°C. while stirring. Stirring is continued at a temperature of 75—80°C. until a sample is insoluble in aqueous diethylamine. Then the reaction mixture is cooled and poured on to ice. The precipitated sulphochloride is filtered off and washed until it gives a neutral reaction. It is added to a solution of 7.84 parts of 1-amino-3-dimethylamino-propane in 8 parts of water while stirring. By following the procedure of Example 1 a clear reddish-blue basic dyestuff is obtained which is readily soluble in dilute acetic acid.

A similar dyestuff may be obtained by using 1-amino-2-dimethylaminoethane as the basic compound.

EXAMPLE 3:

To a solution of 10 parts of the sodium salt of 3,3'-diazacopper phthalocyanine - 4,4'-disulphonic acid (obtained by the reaction of two mols of pyridine-2,3-dicarboxylic acid and two mols of the sodium salt of 4-sulphophthalic acid in a urea melt) in 150 parts of chlorosulphonic acid, 12.4 parts of thionyl chloride are added drop by drop at a temperature of 60—70°C. while stirring. Stirring is continued for 8 hours at 75—80°C. until a sample is insoluble in aqueous diethylamine. After cooling, the reaction mixture is poured on to a mixture of ice and sodium chloride solution. The precipitated sulphochloride is sucked off, mixed with ice-cold sodium chloride solution and neutralized with sodium hydroxide solution. Thereafter 32 parts of 1-diethylamino - 4 - amino-*n*-pentane are added. By following the procedure of Example 1 a reddish-blue basic dyestuff is obtained which is readily soluble in dilute acetic acid.

EXAMPLE 4:

To a solution of 14.3 parts of the sodium salt of 4,4'-diphenyl-copper phthalocyanine-4,4'-disulphonic acid (obtained by the reaction of two mols of diphenyl-3,4-dicarboxylic acid and two mols of the sodium salt of 4-sulphophthalic acid in a urea melt) in 100 parts of chlorosulphonic acid, 24.9 parts of thionyl chloride are added drop by drop at a temperature of 60—70°C. while stirring. Stirring is continued for about 20 minutes at 110°C. until a sample is insoluble in aqueous diethylamine. The reaction mixture is cooled, poured on to ice and the precipitated sulphochloride is filtered off with suction and washed with ice water until it gives a neutral reaction.

The paste obtained is added to a mixture of 19 parts of water, 7.6 parts of sodium bicarbonate and 9.5 parts of 1-amino-3-dimethylamino-propane and stirred for 12 hours at room temperature and for half an hour at 80°C. The precipitated basic dyestuff is filtered off and washed with hot water. It is obtained in nearly quantitative yield and dis-

solves in dilute acetic acid to give a bluish-green solution.

EXAMPLE 5:

To a solution of 10 parts of 4,4',4'',4'''-tetraphenyl-copper phthalocyanine in 100 parts of chlorosulphonic acid 5.5 parts of thionyl chloride are added drop by drop at 20—25°C. while stirring. Stirring is continued for 12 hours at room temperature. The reaction mixture is cooled and poured on to ice. The precipitated sulphochloride is separated by suction and washed with ice water until it gives a neutral reaction. The paste obtained is added to 21.8 parts of 1-diethylamino-4-amino-*n*-pentane and stirred for 12 hours at room temperature and thereafter for one hour at 60°C. The basic dyestuff obtained in good yield is filtered off and washed with water. It dissolves in dilute acetic acid to give a clear green solution.

EXAMPLE 6:

To a solution of 30.4 parts of the sodium salt of cobalt phthalocyanine-4,4',4'',4'''-tetrasulphonic acid in 300 parts of chlorosulphonic acid, 90.3 parts of thionyl chloride are added drop by drop at a temperature of 60—70°C. while stirring. Stirring is continued for 10 hours at 80—90°C. until a sample is insoluble in aqueous diethylamine. After cooling, the reaction mixture is poured on to a mixture of ice and sodium chloride solution. The precipitated sulphochloride is then filtered off with suction and washed with ice water until the filtrate shows a neutral reaction. The neutral paste is added to a mixture of 38 parts of water, 15.2 parts of sodium bicarbonate and 19 parts of 1-amino-3-dimethylamino-propane, stirred for 12 hours at room temperature and for half an hour at 80°C. Upon addition of a small amount of sodium chloride solution the dyestuff is separated by suction and washed with water. It dissolves in dilute acetic acid to give a greenish-blue solution.

A similar dyestuff can be obtained when an equivalent amount of 1-diethylamino-4-amino-*n*-pentane is used instead of the above 1-amino-3-dimethylamino-propane.

EXAMPLE 7:

10 Parts of a copper phthalocyanine, which contains 3 or 4 chloromethyl groups, are dissolved in a mixture of 20 parts of 1-diethylamino-4-amino-*n*-pentane and 20 parts of water, and heated for about 15 hours to 90—95°C. Upon addition of water the precipitated dyestuff is filtered off and washed with water. It is dissolved in 1.5 litres of 3% acetic acid, filtered in the presence of active carbon, and recovered from the solution by the addition of sodium hydroxide solution and filtration. It is soluble in dilute acetic acid to give a clear greenish-blue solution.

EXAMPLE 8:

11.9 Parts of a copper phthalocyanine obtained from diphenylsulphone-3,4-dicarboxylic-acid-3'-sulphonic acid are dissolved in

56 parts of chlorosulphonic acid and reacted with 3.04 parts of thionyl chloride while stirring for 2 hours at 80°C. To obtain the sulphochloride the reaction mixture is cooled and poured on to ice. The precipitate is separated by suction and washed with ice water until the filtrate shows a neutral reaction. The paste of the sulphochloride is mixed with a small amount of 1-amino-2-dimethylamino-ethane. Upon stirring for 10—12 hours at room temperature the excess of 1-amino-2-dimethylamino-ethane is removed by steam distillation and the precipitated basic dyestuff filtered off and washed with hot water. It is obtained in good yield as a clear turquoise dyestuff which is readily soluble in acetic acid.

EXAMPLE 9:

5.87 Parts of 4,4',4'',4'''-tetra-(β -chloroethyl)-phenyl copper phthalocyanine are dissolved in 58.7 parts of chlorosulphonic acid and 7.15 parts of thionyl chloride and stirred for 10—12 hours at room temperature. The sulphochloride is obtained as in the preceding example by pouring the reaction mixture on to ice, filtering off and washing.

The paste of the sulphochloride is mixed with a small amount of ice water and reacted with 10.5 parts of 1-amino-2-dimethylamino-ethane as described in Example 8.

A basic dyestuff of a clear green colour, which is readily soluble in dilute acetic acid, is obtained in good yield.

EXAMPLE 10:

20 Parts of a paste of copper phthalocyanine-(3)-di- and tri-(β -chloroethyl)-sulphonamide containing about 25% of the dyestuff are added to 40 parts of a 50% solution of dimethylamine. Upon addition of 6 parts of a 15% solution of sodium hydroxide the reaction mixture is stirred for 20 hours at room temperature. The reaction product formed is precipitated by heating for a short while and by addition of a solution of sodium acetate. It is filtered off with suction and washed. The dyestuff is obtained in nearly quantitative yield and is soluble in dilute acetic acid to give a clear blue solution.

By using a solution of diethylamine in the above example the corresponding diethylamine derivative is obtained.

The copper phthalocyanine-(3)-di and tri-(β -chloroethyl)-sulphonamide can be obtained by the following procedure:

14.6 Parts of the copper phthalocyanine-(3)-di- and tri-sulphochloride are suspended in 80 parts of water at 5—10°C. To this suspension 7 parts of β -chloroethylamine hydrochloride dissolved in 10 parts of water are added while stirring. Stirring is continued for 4 hours while 39 parts of a 10% solution of sodium hydroxide are added and the temperature gradually rises to 18°C. Thereafter stirring is continued for 20 hours at room temperature. The reaction product obtained in a quantitative yield is filtered off and washed.

EXAMPLE 11:

20 Parts of a paste of copper phthalocyanine-(3)-di- and tri-(β -chloroethyl)-sulphonamide containing 25% of the dyestuff are dissolved in 45 parts of a 50% solution of 1-amino-3-dimethylamino-propane. Upon addition of 6 parts of a 15% solution of sodium hydroxide the reaction mixture is stirred for 20 hours at room temperature. Thereafter a sodium salt solution is added and the dyestuff precipitated by adding hydrochloric acid until the solution becomes neutral. It is soluble in dilute acetic acid to give a clear blue solution.

EXAMPLE 12:

20 Parts of a paste of copper phthalocyanine-(3)-di- and tri-(β , γ -dibromopropyl)-sulphonamide containing 25% of the dyestuff are dissolved in 40 parts of an approximately 50% solution of dimethylamine. Then 9 parts of a 15% solution of sodium hydroxide are added and the reaction mixture is stirred for 20 hours at room temperature. Thereafter the excess of dimethylamine is removed by steam distillation and the dyestuff precipitated by adding sodium chloride solution (and eventually some hydrochloric acid). The reaction product obtained in excellent yield is readily soluble in acetic acid to give a clear blue solution.

The above mentioned copper phthalocyanine-(3)-di- and tri-(β , γ -dibromopropyl)-sulphonamide can be obtained as follows:

14.6 Parts of copper phthalocyanine-(3)-di and tri-sulphochloride are suspended in 50 parts of water at 5—10°C. To this suspension 19 parts of 2,3-dibromopropylamine hydrobromide dissolved in 50 parts of water are added while stirring. Within 4 hours 4.2 parts of a 10% solution of sodium hydroxide are added while the temperature rises to 15°C. The reaction mixture is then stirred for another 20 hours. The reaction product obtained in an excellent yield is separated by suction and washed.

EXAMPLE 13:

20 Parts of a paste of 4,4',4'',4'''-tetra-(p - β -chloroethyl - sulphonamide - phenyl)-copper phthalocyanine containing 25% of the dyestuff are dissolved in 50 parts of an approximately 50% solution of dimethylamine and stirred for 20 hours at room temperature. During this time one part of sodium hydroxide dissolved in a small amount of water is added. Thereafter the excess of dimethylamine is removed, and the dyestuff precipitated by adding sodium acetate solution. It is separated by suction and washed. The basic dyestuff obtained in nearly quantitative yield is soluble in dilute acetic acid to give a clear green solution.

The 4,4',4'',4'''-tetra-(p - β -chloroethyl-sulphonamide-phenyl)-copper phthalocyanine can be obtained as follows:

14.5 Parts of 4,4',4'',4'''-copper phthalocyanine

5 cyanine-tetra-(*p*-phenyl - sulphochloride) are suspended in 80 parts of a mixture of ice and ice water and reacted with 7 parts of β -chloroethylamine hydrochloride dissolved in 10 parts of water at a temperature of 0–5°C. The mixture is stirred for one and a half hours at the same temperature while 4.2 parts of a 10% solution of sodium hydroxide are added. Stirring is then continued at a temperature of 20°C. until the reaction is finished. The dyestuff is separated by suction and washed with water. The yield is quantitative.

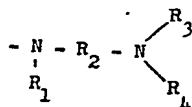
10 Following the procedure of the above example a clear blue basic dyestuff can be obtained from 4,4',4'',4'''-copper phthalocyanine - tetra - (β -chloroethyl)-sulphonamide (obtained from 4,4',4'',4'''-copper phthalocyanine-tetrasulphochloride and β -chloroethylamine).

EXAMPLE 14:

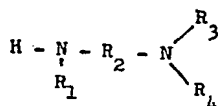
20 5 Parts of copper phthalocyanine-(3)-di- and tri-(β -chloroethyl)-sulphonamide are dissolved in 25 parts of diethanolamine and 20 parts of pyridine. Upon addition of one part of sodium hydroxide dissolved in 6 parts of water the reaction mixture is stirred for 20 hours at room temperature and then for 2 hours at 80–90°C. The basic dyestuff is precipitated by the addition of sodium chloride solution. It is obtained in good yield and dissolves in acetic acid to give a clear blue solution.

What we claim is:—

35 1. A process for the production of basic phthalocyanine dyestuffs having from one to four radicals of the general formula:

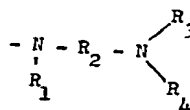


40 attached to a phthalocyanine radical, wherein R_1 is a hydrogen atom or an alkyl radical, R_2 is an acyclic bivalent radical, and R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring, which comprises reacting a phthalocyanine dyestuff which contains one to four replaceable halogen atoms with a tertiary amine of the general formula



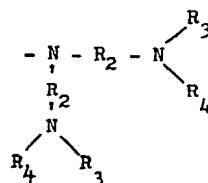
wherein R_1 to R_4 have the aforementioned meanings.

50 2. A process for the production of basic phthalocyanine dyestuffs having from one to four radicals of the general formula:



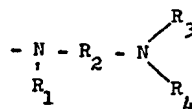
55 attached to a phthalocyanine radical, wherein R_1 is a hydrogen atom or an alkyl radical, R_2 is an acyclic bivalent radical, and R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring, which comprises reacting a phthalocyanine dyestuff which contains one to four replaceable halogen atoms with an aliphatic primary or secondary amine containing at least one halogen atom, and reacting the halogen compound thus obtained with a secondary amine.

3. A process as claimed in claim 2, wherein a basic phthalocyanine dyestuff having from one to four radicals of the general formula



70 attached to a phthalocyanine radical, wherein R_2 is an acyclic bivalent radical, and R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring, is produced by reacting a phthalocyanine dyestuff which contains one to four replaceable halogen atoms with an aliphatic secondary amine containing two halogen atoms, and reacting the halogen compound thus obtained with a secondary amine.

4. A process as claimed in claim 2, wherein the basic dyestuff produced is a dyestuff having from one to four radicals of the general formula



85 attached to a phthalocyanine radical, wherein R_1 , R_3 and R_4 have the meanings specified in claim 2, but R_2 is an acyclic bivalent radical

which contains an $-\text{N} \begin{smallmatrix} \text{R}_3 \\ \diagdown \\ \text{R}_4 \end{smallmatrix}$ radical.

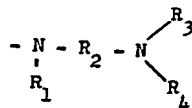
5. A modification of the process claimed in any of claims 1 to 4, wherein in place of said phthalocyanine dyestuff a dyestuff intermediate containing a replaceable halogen atom is used,

and this dyestuff intermediate is converted to the final phthalocyanine upon completion of the process claimed in any of claims 1 to 4.

6. A process as claimed in any of claims 1 to 5, wherein the reaction is carried out in the presence of an acid binding agent.

7. A process as claimed in any of claims 1 to 5, wherein the reaction is carried out in the presence of an inert diluent.

10. 8. A process for the production of basic phthalocyanine dyestuffs having from one to four radicals of the general formula:



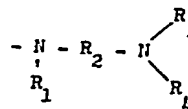
- 15 attached to a phthalocyanine radical, wherein R_1 is a hydrogen atom or alkyl radical or an

$-\text{R}_2-\text{N}<\begin{array}{c} \text{R}_3 \\ \text{R}_4 \end{array}$ group, R_2 is an acyclic bivalent

- radical, and R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring, substantially as described with reference to any of the examples.

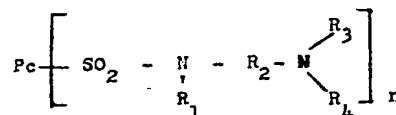
- 20 9. Basic phthalocyanine dyestuffs having from one to four radicals of the general

formula:



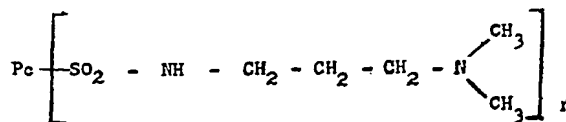
attached to a phthalocyanine radical, wherein R_1 is a hydrogen atom or an alkyl radical, R_2 is an acyclic bivalent radical, and R_3 and R_4 are aliphatic radicals or together with the adjacent nitrogen atom form a heterocyclic ring.

10. Basic phthalocyanine dyestuffs of the general formula:



wherein Pc is the radical of a copper phthalocyanine, R_1 is a hydrogen atom or an alkyl radical, R_2 is an acyclic bivalent radical, R_3 and R_4 are aliphatic radicals or with the adjacent nitrogen atom together form a heterocyclic ring and n is an integer from 1—4.

11. Basic phthalocyanine dyestuffs of the general formula:



- 45 wherein Pc is the radical of a copper phthalocyanine, n is 2 or 3, and the side chains are in the 3-positions of the phthalocyanine molecule.

12. The new basic phthalocyanine dyestuffs described in any of the Examples.

ELKINGTON & FIFE,
Consulting Chemists and
Chartered Patent Agents,
Bank Chambers,

329, High Holborn, London, W.C.1,
Agents for the Applicants.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.